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㉔ **Photochromic ultra-violet ray shield powder, method of manufacturing the same, and skin external preparations using the same.**

㉕ A photochromic ultra-violet ray shield material principally composed of titanium oxide particles, which have a specific surface area of 25 m<sup>2</sup>/g or above and also have  $\Delta E = S \leq A$  (discoloration degrees) and  $B$  (at restoration)  $\leq \Delta E = 3$ , a method of manufacturing the same and a skin external preparation using the same.

Both photochromic property and excellent ultra-violet ray shield effect are obtained.

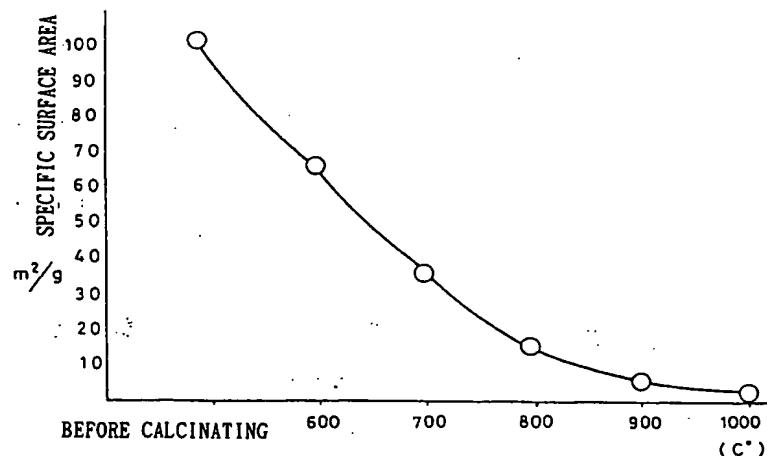


Fig. 1

## [FIELD OF THE INVENTION]

This invention relates to photochromic ultra-violet ray shield powder, method of manufacturing the same and skin external preparation using the same and, more particularly, to imparting ultra-violet ray shield powder, principally composed of titanium oxide, with the photochromic property.

## [BACKGROUND ART]

The property of changing color when one substance is irradiated with light and then returning to its original color when the light irradiation is stopped, is referred to as the photochromic property or phototropic property. This property is utilized for color control glasses or the like containing photochromic materials.

In the field of cosmetics, color variable make-up preparation which utilize the photochromic property and permit enjoyment of color changes, is well known (as disclosed in Japanese Patent Application Laid-Open 49312/1981, Japanese Patent Application Laid-Open 10079/1981 and PCT WO 89/12084), and their applications in broader fields are expected.

Meanwhile, in the field of cosmetics there is problems of adverse effects of ultra-violet rays on the skin, and ultra-violet ray absorbers for absorbing ultra-violet rays and also ultra-violet ray shield powder for shielding ultra-violet rays have been developed.

A typical example of the ultra-violet ray shield powder is fine particle titanium oxide which can scatter ultra-violet rays, and also there is titanium oxide having photochromic property. Therefore, photochromic titanium oxide which has both of these properties has been thought of.

## [SUMMARY OF THE INVENTION]

The present invention has been intended in the light of the above problems in the prior art, and its object is to provide a photochromic ultra-violet ray shield powder, which has both ultra-violet ray shield effect and excellent photochromic property.

To attain the above object of the invention, the inventors have conducted extensive researches and investigations conditions for imparting fine particle titanium oxide with the photochromic property and agglomeration properties. They found that powder having excellent photochromic property and ultra-violet ray shield effect could be obtained by manufacturing it under specific conditions in correspondence to the specific surface area of the material fine particle titanium oxide. The invention is completed on the basis of this finding.

According to claim 1 of the present application, there is provided a photochromic ultra-violet ray shield powder principally composed of particles with specific surface area of  $25 \text{ m}^2/\text{g}$  or above and  $A \geq 5$  and  $B \leq 3$ ,  $A$  and  $B$  being determined as follows.

4 g of the powder is uniformly dispersed in 16 g of nitrocellulose lacquer to form a dispersion, which is coated on art paper using an applicator to form a coating film with thickness of  $76 \mu\text{m}$ , which coating film is in turn dried to be used as a sample for photochromic property measurement under an optical condition that a lamp ("FL20S, BLB" manufactured by Toshiba) and a lamp ("FL20S, E" manufactured by Toshiba) are secured at a distance of 11 cm from each other. Distance adjustment of the sample is effected using an ultra-violet ray intensity measuring apparatus ("SUV-T" manufactured by Tolay Techno) such that the intensity of ultra-violet rays incident on the sample is  $2 \text{ mW/cm}^2$ .

(1) The sample is colorimetrically measured after it has been left at room temperature and in a dark place for about 10 hours, the measurement being made using a colorimeter ("CR-200" manufactured by Minolta).

(2) The sample is immediately colorimetrically measured when it is darkened by irradiation with the ultra-violet rays for 30 minutes in same way as described above.

(3) The irradiated sample is similarly colorimetrically measured after leaving it at room temperature and in a dark place for 24 hours.

A represent the color difference  $\Delta E$  between the color determined in (1) and the color determined in (2).

B represents the color difference  $\Delta E$  between the color determined in (1) and the color determined in (3).

According to claim 2, there is provided photochromic ultra-violet ray shield powder, which is principally composed of titanium oxide.

According to claim 3, there is provided photochromic ultra-violet ray shield powder, which contains at least 50 % of anatase type titanium oxide.

According to claim 4, there is provided photochromic ultra-violet ray shield powder, which contains a photochromic property imparting agent metal Me such that

$$0.05 \geq \text{MeO}_m / (\text{MeO}_m + \text{TiO}_2) \geq 0.0001$$

5 m = 1/2, 1, 3/2, 2 or 3.

According to claim 5, there is provided a photochromic ultra-violet ray shield powder obtainable by calcinating material titanium oxide with a specific surface area of 100 m<sup>2</sup>/g or above at a temperature of 700 °C or below.

10 According to claim 6, there is provided a method of manufacturing photochromic ultra-violet ray shield powder, which comprises the step of calcinating material titanium oxide with a specific surface area of S<sub>0</sub> m<sup>2</sup>/g (S<sub>0</sub> being 100 or above) at a temperature of T °C calculated by relations (1) below;

Relations (1):

15 T = (S<sub>0</sub> + 10)/0.10

400 ≤ T ≤ 600

According to claim 7, there is provided a method of manufacturing photochromic ultra-violet ray shield powder, in which the photochromic property imparting agent metal being in the form of salt or alkoxide and 20 precipitated by solution of the salt or the alkoxide by neutralization or hydrolysis reaction.

According to claim 8, there is provided a method of manufacturing photochromic ultra-violet ray shield powder, the pH is controlled to 8 to 11 during the neutralization.

According to claim 9, there is provided a skin external preparation containing 0.1 to 60 % by weight of the photochromic ultra-violet ray shield powder.

25 Now, the constitution of the invention will be described in detail.

Titanium oxide used as material according to the invention may be titanium dioxide, lower titanium oxide, etc. These titanium oxide varieties may be used in combinations. Titanium dioxide may be of anatase type, rutile type and amorphous. Any of these varieties may be used. Suitably, at least 50 % of anatase type titanium oxide may be contained because in this case satisfactory photochromic property can be 30 obtained. The particles may be indefinite, flaky or spherical in shape.

The material titanium oxide used according to the invention may be those obtained by a gaseous phase process, a liquid phase process and various other processes.

The gaseous phase process is one, in which halotitanium in the form of vapor or gas is decomposed at a high temperature together with an oxidizing agent or a hydrolysis agent to obtain titanium oxide.

35 The liquid phase process is one, in which titanium tetra-isopropoxide or the like subjected to hydrolysis to obtain titanium oxide.

The size of the titanium oxide particles after calcinating is suitably 25 m<sup>2</sup>/g or above, preferably 40 to 100 m<sup>2</sup>/g, in terms of the specific surface area. If the size is less than 25 m<sup>2</sup>/g or greater than 100 m<sup>2</sup>/g, the ultra-violet ray shield effect tends to be reduced.

40 The proportion of titanium oxide used in the manufacture of photochromic line particle titanium oxide, is suitably 95.0 to 99.99 % by weight.

Examples of the metal used to impart titanium oxide with the photochromic property, are iron, zinc, aluminum, silicon, etc. These metals may be used in the form of their powder or as their salts, e.g., sulfates, chlorides, nitrates and acetates, or oxides, hydrates, hydroxides, etc. The photochromic property may also 45 be imparted using cobalt, cerium, etc. In this case, however, the powder itself is colored, undesirably making it difficult in actual practice to observe the photochromic property.

Particularly, metallic iron powder and iron compounds are suitable from the standpoints of the safety in human use and imparting with the photochromic property. According to the invention, metallic iron powder and iron compounds may be used alone or in their suitable combinations. Examples of the iron compound 50 are salts of iron, e.g., iron sulfate, iron chloride, iron nitrate, iron acetate, etc., and also iron oxide and iron hydroxide.

The proportion of the metal used to impart with the photochromic property in the manufacture of photochromic titanium oxide, is suitably 0.1 to 5.0 % by weight, preferably 0.5 to 1.5 % by weight. If the proportion of the metal is insufficient, it is liable to result in insufficient photochromic property. If the 55 proportion is excessive, on the other hand, undesired coloring is liable.

Further, according to the invention it is possible to compound the photochromic ultra-violet ray shield powder with other inorganic or organic compounds. For example, the photochromic fine particle titanium oxide may be mixed with or compounded by means of coating or calcinating with one or more members of

the group consisting of inorganic compounds, e.g., mica, sericite, talc, kaolin, silica, barium sulfate, iron oxide, chromium oxide, copper oxide, nickel oxide, vanadium oxide, manganese oxide, cobalt oxide, calcium oxide, magnesium oxide, molybdenum oxide, zinc oxide, iron, chromium, copper, nickel, vanadium, manganese, etc., and organic compounds, e.g., nylon, polymethyl methacrylate, polystyrene, epoxy resins, polyethylene, etc.

5 Further, ordinary titanium oxide may be compounded with other inorganic or organic compounds to impart with the photochromic property.

10 A composite material containing photochromic titanium oxide may be obtained by adding 0.1 to 0.5 % by weight of metallic iron particles or iron compounds to a composite material such as titanium-mica or titanium-talc coated with titanium dioxide by a dry process using a ball mill or the like or by a wet process of adding the system in the form of an aqueous solution and then calcinating the resultant system. In an alternative method, a titanium dioxide composite material by means of the hydrolysis of titanyl sulfate in the presence of metallic iron powder or iron compounds and then calcinated.

15 According to the invention, the composite material containing photochromic titanium oxide may be used after subjecting it to surface treatment, e.g., silicone treatment, surfactant treatment, surface alkoxy treatment, metallic soap treatment, fatty acid treatment, fluorine resin treatment, wax treatment, etc. By improving the dispersion property in this way, it is possible to further improve the ultra-violet ray shield performance and photochromic property.

20 When using the photochromic ultra-violet ray shield powder for a skin external preparation, its proportion in the total composition is suitably 1.0 to 60.0 % by weight, preferably 5.0 to 20.0 % by weight. If the proportion is less than 1 % by weight, the color change function may not be provided. If the proportion is over 30 % by weight, on the other hand, the color change degree may often be excessive.

25 When flaky titanium oxide is used to manufacture the photochromic ultra-violet ray shield powder, the proportion in the total composition is suitably 10 to 60 % by weight, preferably 10 to 40 % by weight. The reason for increasing the proportion compared to the case of using the fine particle titanium oxide as the material, is that the color change degree per unit weight is reduced with increased particle size of the flaky titanium oxide.

30 Likewise, when incorporating the fine particle photochromic ultra-violet ray shield powder is incorporated in a foundation or a powdery make-up preparation such as loose powder or pressed powder, it is suitably incorporated in 1 to 30 % by weight. If its content is less than 1 % by weight, sufficient photochromic property can not be obtained. If the content is over 30 % by weight, on the other hand, excessive color tone change is liable.

35 When using flaky titanium oxide as titanium oxide, it is suitably incorporated by 10 to 60 % by weight with respect to powdery cosmetics.

When the fine particle photochromic titanium oxide in liquid cosmetics such as sun oil, it is suitably incorporated in 1 to 30 % by weight.

40 If the proportion exceeds 30 % by weight, the viscosity will be excessively increased, and in this case it is difficult to provide the function of the liquid cosmetics.

The composition incorporating the photochromic ultra-violet ray shield powder according to the invention, may suitably incorporate, if desired, other components usually used for the compositions of cosmetics or the like. For example, it may incorporate inorganic powder, e.g., talc, kaolin, mica, sericite, white mica, gold mica, synthetic mica, red mica, black mica, rithia mica, vermicurite, magnesium carbonate, calcium carbonate, diatomaceous earth, magnesium silicate, calcium silicate, aluminum silicate, barium silicate, barium sulfate, strontium silicate, tungstate metal salts, silica, magnesium oxide, calcium oxide, 45 zeolite, boron nitride, ceramic powder, etc., organic powder, e.g., nylon powder, polyethylene powder, benzoguanamine powder, tetrafluoroethylene powder, fine crystalline cellulose, etc., inorganic white pigments, e.g., titanium dioxide, zinc oxide, etc., inorganic red pigments, e.g., iron oxide (red iron oxide), iron titanate, etc., inorganic brown pigments, e.g.,  $\gamma$ -iron oxide, etc., inorganic yellow pigments, e.g., yellow iron oxide, loess, etc., inorganic black pigments, e.g., black iron oxide, carbon black, etc., inorganic violet 50 pigments, e.g., mango violet, cobalt violet, etc., inorganic green pigments, e.g., chromium oxide, chromium hydroxide, cobalt titanate, etc., inorganic blue pigments, e.g., ultramarine, red marine, etc., pearl pigments, e.g., mica coated with titanium dioxide, bismuth oxychloride coated with titanium dioxide, bismuth oxychloride, talc coated with titanium oxide, mica coated with colored titanium oxide, etc., metal powder pigments, e.g., aluminum powder, copper powder, etc., such organic pigments as "Red No. 201", "Red No. 202", "Red NO. 204", "Red No. 205", "Red No. 120", "Red No. 226", "Red No. 228", "Red No. 405", "Orange No. 203", "Orange No. 204", "Yellow No. 205", "Yellow No. 401", "Blue No. 404", etc, and such organic pigments as "Red No. 3", "Red No. 104", "Red No. 106", "Red No. 227", "Red No. 230", "Red No. 401", "Red No. 505", "Orange No. 205", "Yellow No. 5", "Yellow No. 202", "Yellow No. 203", "Green

No. 3", "Blue No. 1", zirconium, barium, aluminum lake, etc., natural dyestuffs. e.g., chlorophyll,  $\beta$ -kalotin, etc., various hydrocarbons, e.g., squalane, liquid paraffin, vaseline, microcrystalline wax, ozokelite, serecine, cetylalcohol, hexadecylalcohol, oleilalcohol, cetyl-2-ethyl hexanoate, 2-ethylhexyl permiate, 2-octyldodecyl myristate, 2-octyldodecylgum ester, neopentylglycol-2-ethyl hexanoate, triglyceril iso-octanoate, 2-octyl-dodecyl oleate, iso-propyl myristate, triglyceril iso-stearate, coconut oil fatty acid triglyceride, olive oil, avocade oil, bees wax, myristyl myristate, mink oil, ranoline, dimethylpolysiloxane etc., oil, e.g., fat and oil, esters, higher alcohols, solders, silicone oil, etc., ultra-violet ray absorbers, anti-oxidization agents, surface active agents, moisture retainers, perfumes, water, alcohol and viscosity increasing agents.

When the photochromic ultra-violet ray shield power according to the invention is used for a cosmetics, 10 the cosmetics may be powdery, cake-like, pencil-like, stick-like, paste-like, liquid-like, emulsion-like, cream-like, etc.

With the use of the photochromic flaky titanium oxide, molding surface may be removed with puff with difficulty of caking. In addition, the slip can be improved when the cosmetics is applied to the skin, thus improving the property of use of the make-up preparation.

15 As shown, according to the invention by incorporating the photochromic ultra-violet ray shield powder in compositions, typically cosmetics, it is possible to obtain photochromic property, which could not have been attained with the prior art materials of cosmetics products. Besides, because of high ultra-violet ray shield effect, it is possible to eliminate adverse effects of excessive ultra-violet rays on the skin. Further, the composition is highly stable with respect to light, and it does not cause any fatigue phenomenon. Thus, it is 20 possible to obtain stable products.

Further, photochromic titanium oxide is far more stable than photochromic organic materials.

The photochromic ultra-violet ray shield powder may be used for paints as well as for cosmetics.

#### [BRIEF DESCRIPTION OF THE DRAWINGS]

25 Fig. 1 is a graph showing the relation between the specific surface area and calcinating temperature of titanium oxide;  
 Fig. 2 is a view illustrating a process of manufacture of photochromic titanium oxide by a neutralization process;  
 30 Fig. 3 is a view illustrating a process of manufacture of photochromic titanium oxide by a urea process;  
 Fig. 4 is a graph showing the relation between the specific surface area and calcinating temperature of titanium oxide samples having different specific surface areas; and  
 Figs. 5 to 8 are graphs showing ultra-violet ray shield effects of photochromic ultra-violet ray shield powder according to the invention.

#### [BEST MODE FOR CARRYING OUT THE INVENTION]

Now, preferred mode of carrying out the invention will be described with reference to the drawings, without any sense of limiting the invention. Proportions are shown in % by weight if they are not particularly 40 specified.

##### Definition of the photochromic property

According to the invention, the photochromic property is tested as follows.

45 4g of photochromic ultra-violet ray shield powder is uniformly dispersed in 16g of nitrocellulose lacker to form a dispersion. The dispersion is coated on art paper using an applicator to form a coating film with thickness of 76  $\mu$ m. The coating film is then dried and used as a sample for photochromic property measurement under an optical condition that a lamp ("FL20.BLB" manufactured by Toshiba) and a lamp ("FL20S.E" manufactured by Toshiba) are secured at a distance of 11 cm from each other. Distance 50 adjustment of the sample is effected using an ultra-violet ray intensity measuring apparatus ("SUV-T" manufactured by Tolay Techno) such that the intensity of ultra-violet rays incident on the same is 2 mW/cm<sup>2</sup>.

Actual colorimetric measurements are done as follows:

55 (1) The sample is colorimetrically measured after it has been left at room temperature and in a dark place for about 10 hours, the measurement being made using a colorimeter ("CR-200" manufactured by Minolta).  
 (2) The sample is immediately colorimetrically measured when it is darkened by irradiation with the ultra-violet rays for 30 minutes in same way described above.

(3) The irradiated sample is similarly colorimetrically measured after leaving it at room temperature and in a dark place for 24 hours. The photochromic property is defined as

5  $5 \leq A$ , and

B  $\leq 3$ ,

10 where A represents the color difference  $\Delta E$  between the color determined in (1) and the color determined in (2), and B represents the color difference  $\Delta E$  between the color determined in (1) and the color determined in (3).

15 Relation between specific surface area and calcinating temperature

In order to study for the cause of reduction of the ultra-violet ray shield effect of titanium oxide powder having ultra-violet ray shield effect as a result of imparting the powder with the photochromic property, the inventors examined the relation between the specific surface area and calcinating temperature.

15 The titanium oxide having specific surface area of 98 m<sup>2</sup>/g was calcinated at 600 to 1,000°C and the specific surface area after the calcinating was measured.

Results as shown in Table 1 and Fig. 1 were obtained.

20

Table 1

Calcinating temperature	Specific surface area (m <sup>2</sup> /g)
Before calcinating	98
600	66.3
700	36.9
800	15.5
900	6.0
1,000	3.5

25

It will be understood from Table 1 above that with the increase the calcinating temperature the specific surface area is reduced, while the particle size is increased.

30 In this way, with reduction of the specific surface area, i.e., with increase of the particle size, the ultra-violet ray shield effect of fine particle titanium oxide powder is reduced.

35 Meanwhile, in the prior art for imparting titanium oxide with the photochromic property, calcinating at about 600°C or above is usually required, and photochromic ultra-violet ray shield powder having satisfactory photochromic property and satisfactory ultra-violet ray shield effect has not been obtained.

40 The inventors, accordingly, conducted further investigations about the photochromic property of fine particle titanium oxide.

Relation between the photochromic property and manufacture method thereof

The photochromic property is influenced by the method of manufacture.

45 Typical processes of imparting titanium oxide with the photochromic property are a neutralization process and an urea process.

Neutralization process

50 In the neutralization process, as shown in Fig. 2, titanium oxide is dispersed in deionized water, and the dispersion is stirred with iron chloride  $FeCl_3$  added to it. The system is then neutralized by adding sodium hydroxide, and reacted at 80 to 90°C for 2 hours. The reacted system is then filtered, and the residue is washed with water, then dried, then calcinated and then disintegrated.

55 Photochromic property is shown as color difference  $\Delta E$  in case of using rutile type titanium oxide as titanium oxide in Table 2, and in case of using anatase type titanium oxide in Table 3.

The restoration factor is given as:

$(\Delta E \text{ after ultra-violet ray irradiation} - \Delta E \text{ after leaving in dark place}) / (\Delta E \text{ after ultra-violet ray irradiation})$

The symbols shown under the numerical values of  $\Delta E$  after ultra-violet ray irradiation for 30 minutes and  $\Delta E$  after leaving in dark place for 24 hours concern judgment as to whether the values meets the

definition noted above of the photochromic property. (O; meets, Δ; substantially meets, ×; fails to meet)

5 Table 2  
Neutralization process  
(rutile type, specific surface area: 98 m<sup>2</sup>/g, 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800	900
ΔE after ultra-violet ray irradiation for 30 minutes	3.44	3.37	2.96	2.63	2.81
(A)	×	×	×	×	×
ΔE after leaving in dark place for 60 minutes	2.13	2.03	1.63	1.88	1.00
Restoration factor	38 %	40 %	45 %	29 %	65 %
ΔE after leaving in dark place for 24 hours	0.98	0.88	0.93	1.04	0.51
(B)	○	○	○	○	○
Restoration factor	78 %	74 %	69 %	61 %	82 %

30 Table 3  
Neutralization process  
(anatase type, 98 m<sup>2</sup>/g, 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800	900
ΔE after ultra-violet ray irradiation for 30 minutes	6.61	8.16	8.83	7.00	5.75
(A)	○	○	○	○	○
ΔE after leaving in dark place for 60 minutes	3.65	5.76	6.66	5.95	2.34
Restoration factor	45 %	30 %	25 %	15 %	60 %
ΔE after leaving in dark place for 120 minutes	3.07	5.02	6.09	5.52	2.17
Restoration factor	54 %	39 %	32 %	22 %	63 %
ΔE after leaving in dark place for 24 hours	1.88	3.15	3.96	4.02	1.45
Restoration factor	72 %	62 %	56 %	43 %	75 %

When the material titanium oxide used under the above conditions is rutile type, the color change degree is small, and substantially sufficient photochromic property can not be obtained.

When the anatase type is used, the photochromic property can be extremely improved compared to the case of using the rutile type. Also, the color change degree is large, i.e., 660 to 700°C. However, it is 5 suitably about 600°C when the restoration factor is also taken into considerations.

Concerning the neutralization process, it is thought that the photochromic property is influenced by the pH at the time of the neutralization.

Accordingly, the inventors conducted researches of the photochromic property with different pH settings in the neutralization process. Tables 4 to 6 show the results.

10

Table 4  
Neutralization process  
pH: 8 (anatase type, specific surface area: 98 m<sup>2</sup>/g, 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800
ΔE after ultra-violet irradiation for 30 minutes (A)	8.03	10.00	11.00	9.46
○ ○ ○ ○				
ΔE after leaving in dark place for 60 minutes	4.73	7.57	8.99	7.90
Restoration factor	42 %	25 %	19 %	17 %
ΔE after leaving in dark place for 24 hours (B)	2.68	5.01	6.34	5.57
○ × × ×				
Restoration factor	67 %	50 %	43 %	33 %

35

Table 5  
Neutralization process  
pH: 9 (anatase type, specific surface area: 98 m<sup>2</sup>/g, 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800
ΔE after ultra-violet ray irradiation for 30 minutes	6.31	7.61	9.59	4.59

45

50

55

(A)	○	○	○	△
ΔE after leaving in dark place for 60 minutes	3.07	5.06	5.54	3.51
Restoration factor	52 %	34 %	43 %	24 %
ΔE after leaving in dark place for 24 hours	1.71	3.08	3.66	2.42
(B)	○	△	△	○
Restoration factor	73 %	60 %	62 %	48 %

15 Table 6  
Neutralization process  
pH: 10 (anatase type, 98 m<sup>2</sup>/g, 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800
ΔE after ultra-violet irradiation for 30 minutes	6.17	7.05	8.09	5.28
(A)	○	○	○	○
ΔE after leaving in dark place for 60 minutes	2.70	4.24	5.73	4.26
Restoration factor	57 %	40 %	30 %	20 %
ΔE after leaving in dark place for 24 hours	1.25	2.30	3.48	2.78
(B)	○	○	△	○
Restoration factor	80 %	68 %	57 %	48 %

40 As is clear from Tables 4 to 6, by using anatase type titanium oxide, satisfactory color change degree can be obtained with any of the pH 8 to 10. Considering the restoration factor, however, lower calcinating temperature is rather satisfactory. The color change degree is most satisfactory with pH 8. On the other hand, the restoration factor is the better the higher pH.

45 The relation between the photochromic factor and pH was studied similarly in the case of using titanium oxide with anatase/rutile = 75/25 as material.

Rutile type titanium oxide has a large refractive index and said to have greater ultra-violet ray shield effect than anatase type titanium oxide provided the particle size is the same. Therefore, when the ultra-violet ray shield effect is considered, it is suitable to incorporate rutile type titanium oxide.

Accordingly, researches were conducted on the influence of incorporating rutile type titanium oxide in anatase type titanium oxide on the photochromic property.

Results are shown in Tables 7 to 9.

5  
 Table 7  
 Neutralization process  
 pH: 8 (anatase/rutile = 75/25 48 m<sup>2</sup>/g, 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

	Calcinating temperature	600	660	700	800
10	ΔE after ultra-violet ray irradiation for 30 minutes (A)	5.13	5.07	3.86	1.76
15	ΔE after leaving in dark place for 60 minutes	3.03	3.14	2.52	1.32
20	Restoration factor	41 %	39 %	35 %	25 %
25	ΔE after leaving in dark place for 120 minutes	2.78	2.67	2.23	1.22
30	Restoration factor	46 %	48 %	42 %	31 %
35	ΔE after leaving in dark place for 24 hours (B)	1.08	0.73	0.36	0.52
40	Restoration factor	79 %	86 %	91 %	70 %

Table 8  
Neutralization process  
pH: 9 (anatase/rutile = 75/25 48 m<sup>2</sup>/g. 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800
$\Delta E$ after ultra-violet ray irradiation for 30 minutes	4.92	4.30	4.57	1.26
(A)	$\Delta$	$\Delta$	$\Delta$	$\times$
$\Delta E$ after leaving in dark place for 60 minutes	2.99	2.30	2.99	0.80
Restoration factor	40 %	47 %	35 %	37 %
$\Delta E$ after leaving in dark place for 120 minutes	2.55	1.95	2.60	0.68
Restoration factor	48 %	55 %	43 %	46 %
$\Delta E$ after leaving in dark place for 24 hours	1.01	0.48	1.01	0.11
(B)	$\circ$	$\circ$	$\circ$	$\circ$
Restoration factor	80 %	89 %	78 %	91 %

Table 9  
Neutralization process  
pH: 10 (anatase/rutile = 75/25 48 m<sup>2</sup>/g. 0.7% Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800
$\Delta E$ after ultra-violet ray irradiation for 30 minutes	4.89	4.42	5.16	1.36
(A)	$\Delta$	$\Delta$	$\circ$	$\times$
$\Delta E$ after leaving in dark place for 60 minutes	2.59	2.42	3.32	0.76
Restoration factor	48 %	45 %	36 %	44 %
$\Delta E$ after leaving in dark place for 120 minutes	2.16	1.94	2.99	0.67
Restoration factor	56 %	56 %	42 %	51 %
$\Delta E$ after leaving in	0.94	0.70	1.16	0.16

dark place for 24 hours	
(B)	○ ○ ○ ○
Restoration factor	81 % 84 % 78 % 88 %

5

As is clear from Tables 7 to 9, the rutile type incorporated reduces the color change degree but provides for satisfactory restoration factor. It is also to be understood that both the color change degree and restoration degree are satisfactory in the neighborhood of pH 8.

10 In the overall consideration of the above, it will be understood that when using the neutralization process it is suitable to use 75 % or more of anatase type titanium oxide and effect a treatment about pH 8.

#### Urea process

15 The urea process is usually said be based on mild conditions of reaction, and it is possibly effective for prevention of the aggregation of titanium oxide.

In the urea process, as shown in Fig. 3, titanium oxide is dispersed in deionized water, and the system is stirred together with added iron chloride  $FeCl_3$ . Then, 5 % sodium hydroxide aqueous solution was added for neutralization. Then, urea is added, and the resultant system is reacted at 90 to 98 °C for 3 hours. Then, 20 the reacted system is filtered, and the residue is washed with water, then dried, then calcinated and then disintegrated.

Tables 10 and 11 below show the photochromic property in terms of the color difference  $\Delta E$ , respectively when rutile type titanium oxide is used as titanium oxide and when anatase type titanium oxide is used.

25

Table 10

Urea process  
(rutile type, specific surface area:  $98 \text{ m}^2/\text{g}$ , 0.5 %  $Fe_2O_3$ )

	Calcinating temperature	600	660	700	800	900
30	$\Delta E$ after ultra-violet ray irradiation for 30 minutes (A)	2.84	2.92	2.66	2.19	2.91
35	×	×	×	×	×	
40	$\Delta E$ after leaving in dark place for 60 minutes Restoration factor	1.39	1.77	1.35	1.35	0.77
45	52 %	40 %	50 %	39 %	74 %	
	$\Delta E$ after leaving in dark place for 24 hours Restoration factor	0.98	0.80	0.57	0.60	0.45
	66 %	73 %	79 %	73 %	85 %	

50 With rutile type titanium oxide used as material, the color change degree is small, and sufficient photochromic property can not be provided. The color change degree and restoration factor are thought to be independent of the calcinating temperature.

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Table 11  
Urea process  
(anatase type 98 m<sup>2</sup>/g, 0.5 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	600	660	700	800	900
ΔE after ultra-violet irradiation for 30 minutes (A)	7.83	7.89	7.74	6.58	2.54
○ ○ ○ ○ ×					
ΔE after leaving in dark place for 60 minutes Restoration factor	3.26	4.19	5.18	5.54	1.16
59 % 47 % 34 % 16 % 54 %					
ΔE after leaving in dark place for 120 minutes Restoration factor	2.49	3.61	5.01	5.23	1.04
69 % 55 % 36 % 21 % 59 %					
ΔE after leaving in dark place for 24 hours (B)	1.69	2.14	3.24	3.95	0.69
○ ○ △ △ ○					
Restoration factor	79 %	73 %	59 %	40 %	73 %

With anatase type titanium oxide used as the material, the lower the calcinating temperature the greater the color change degree, as is seen from Table 11. In addition, the restoration factor is the better the lower the calcinating temperature.

Further, in comparison to Table 3, the color change degree is great and also the restoration factor is satisfactory in a low calcinating temperature range.

It will be understood from the above that calcinating at a temperature lower than the common sense calcinating temperature in the prior art is effective for imparting fine particle titanium oxide with the photochromic property.

The fact that it is possible to obtain satisfactory photochromic property at a low temperature, is very useful in view of the prevention of the aggregation during calcinating.

Accordingly, the inventors conducted further researches concerning the photochromic property in a low calcinating temperature range.

#### Low temperature range calcinating and photochromic property

The inventors conducted researches concerning the relation between the low temperature calcinating and photochromic property.

#### Neutralization process

Table 12  
 Neutralization process  
 pH: 8 (anatase type, specific surface area: 98 m<sup>2</sup>/g, Fe<sub>2</sub>O<sub>3</sub> 0.7 %)

Calcinating temperature	560	580
ΔE after ultra-violet ray irradiation for 30 minutes (A)	7.16	7.38
	○	○
ΔE after leaving in dark place for 60 minutes	3.47	4.18
Restoration factor	52 %	44 %
ΔE after leaving in dark place for 120 minutes	2.80	3.59
Restoration factor	61 %	52 %
ΔE after leaving in dark place for 24 hours (B)	1.58	2.21
Restoration factor	78 %	71 %

Table 13  
 Neutralization process  
 pH: 9 (anatase type, specific surface area: 98 m<sup>2</sup>/g, Fe<sub>2</sub>O<sub>3</sub>: 0.7 %)

Calcinating temperature	560	580
ΔE after ultra-violet ray irradiation for 30 minutes (A)	6.13	5.80
	○	○
ΔE after leaving in dark place for 60 minutes	2.26	2.46
Restoration factor	64 %	57 %
ΔE after leaving in dark place for 120 minutes	1.75	2.05
Restoration factor	72 %	65 %

5	$\Delta E$ after leaving in dark place for 24 hours (B)	0.93	1.18	○	○
	Restoring factor	85 %	80 %		

10 Table 14  
Neutralization process  
pH: 10 (anatase type, specific surface area: 98 m<sup>2</sup>/g, Fe<sub>2</sub>O<sub>3</sub>: 0.7 %)

15	Calcinating temperature	560	580		
20	$\Delta E$ after ultra-violet ray irradiation for 30 minutes (A)	6.26	7.02	○	○
25	$\Delta E$ after leaving in dark place for 60 minutes Restoration factor	2.10	3.26	67 %	54 %
30	$\Delta E$ after leaving in dark place for 120 minutes Restoration factor	1.35	2.75	79 %	61 %
35	$\Delta E$ after leaving in dark place for 24 hours (B)	0.60	1.76	○	○
	Restoration factor	90 %	75 %		

40 It will be understood from the above that by using the neutralization process with anatase type titanium oxide as material, sufficient photochromic property can be obtained at 560 to 580 °C, which is lower than the temperature of 600 °C thought to be necessary for imparting with the photochromic property in prior art.

45 Further researches were conducted in case of incorporating rutile type titanium oxide.

Table 15

Neutralization process  
(anatase/rutile = 75/25, specific surface area: 48 m<sup>2</sup>/g, Fe<sub>2</sub>O<sub>3</sub>: 1.0 %)

	Calcinating temperature	560	600	660	700
5	ΔE after ultra-violet ray irradiation for 30 minutes (A)	5.29	5.62	5.38	5.02
10	○ ○ ○ ○				
15	ΔE after leaving in dark place for 60 minutes Restoration factor	3.52	3.34	3.64	3.32
20	33 % 41 % 32 % 34 %				
25	ΔE after leaving in dark place for 120 minutes Restoration factor (B)	2.56	2.91	3.06	2.89
30	52 % 48 % 43 % 42 %				
35	ΔE after leaving in dark place for 24 hours Restoration factor	1.30	1.26	1.44	1.44
40	○ ○ ○ ○				
45	75 % 78 % 73 % 71 %				

Table 16

Neutralization process  
(anatase/rutile = 75/25, specific surface area: 48 m<sup>2</sup>/g, Fe<sub>2</sub>O<sub>3</sub>: 2.0 %)

	Calcinating temperature	560	600	660	700
35	ΔE after ultra-violet ray irradiation for 30 minutes (A)	3.72	3.87	3.53	3.15
40	× × × ×				
45	ΔE after leaving in dark place for 60 minutes	2.41	2.45	2.43	1.93
50	120 minutes	1.85	2.11	2.16	1.70
55	24 hours	0.97	1.18	1.20	0.94

50 As is seen from Tables 15 and 16, where rutile type titanium oxide is incorporated by 25 %, satisfactory photochromic property can be obtained at 560 to 700 °C with Fe<sub>2</sub>O<sub>3</sub> provided by 1.0 %. With Fe<sub>2</sub>O<sub>3</sub> provided by 2.0 %, however, the photochromic property is rather deteriorated.

55 Researches were conducted concerning low temperature calcinating using the urea process. Tests were conducted by using anatase/rutile = 50/50 as material titanium oxide and varying the amount of Fe<sub>2</sub>O<sub>3</sub>.

Table 17

5 Urea process  
 (anatase/rutile = 50/50, specific surface area: 98 m<sup>2</sup>/g. Fe<sub>2</sub>O<sub>3</sub>: 0.7 %)

Calcinating temperature	560	600	660	700
ΔE after ultra-violet ray irradiation for 30 minutes (A)	4.58	4.76	4.74	6.46
△ △ △ ○				
ΔE after leaving in dark place for 60 minutes	1.39	1.62	2.60	4.58
Restoration factor	70 %	66 %	46 %	30 %
△ E after leaving in dark place for 120 minutes	1.26	1.37	2.14	4.11
Restoration factor	73 %	72 %	55 %	37 %
△ E after leaving in dark place for 24 hours (B)	1.02	1.01	1.02	2.47
○ ○ ○ ○				
Restoration factor	78 %	79 %	79 %	62 %

Table 18

30 35 Urea process  
 (anatase/rutile = 50/50, specific surface area: 98 m<sup>2</sup>/g. Fe<sub>2</sub>O<sub>3</sub>: 1.5 %)

Calcinating temperature	560	600	660	700
△E after ultra-violet ray irradiation for 30 minutes (A)	5.36	5.75	6.10	8.06
○ ○ ○ ○				

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5	ΔE after leaving in dark place for 60 minutes	1.87	2.65	3.62	6.05
	Restoration factor	66 %	54 %	41 %	25 %
10	ΔE after leaving in dark place for 120 minutes	1.48	2.21	3.15	5.48
	Restoration factor	73 %	62 %	49 %	33 %
15	ΔE after leaving in dark place for 24 hours	0.94	1.17	1.78	3.56
	(B)	○	○	○	△
	Restoration factor	83 %	80 %	71 %	42 %

Table 19

Urea process

(anatase/rutile = 50/50, specific surface area: 98 m<sup>2</sup>/g, Fe<sub>2</sub>O<sub>3</sub>: 3.0 %)

20	Calcinating temperature	560	600	660	700
25	ΔE after ultra-violet ray irradiation for 30 minutes	4.44	4.45	5.62	6.61
	(A)	△	△	○	○
30	ΔE after leaving in dark place for 60 minutes	1.87	1.78	3.52	5.15
	Restoration factor	58 %	60 %	38 %	23 %
35	ΔE after leaving in dark place for 120 minutes	1.54	1.41	3.28	4.68
	Restoration factor	66 %	69 %	42 %	30 %
40	ΔE after leaving in dark place for 24 hours	0.89	0.66	2.09	3.50
	(B)	○	○	○	△
45	Restoration factor	80 %	86 %	63 %	48 %

As is seen from the above, where anatase/rutile = 50/50 is used as material titanium oxide for manufacture with the urea process, the color change degree is rather small if the calcinating is effected in a low temperature range. However, by slightly increasing the content of iron as active agent (i.e., Fe<sub>2</sub>O<sub>3</sub>: 1.5 %), satisfactory photochromic property can be obtained at 560 to 700 °C.

As shown above, it was made clear that so far as fine particle titanium oxide is concerned sufficient photochromic property could be obtained at a calcinating temperature lower than the common sense calcinating temperature in the prior art.

55 The inventors further tried calcinating at 400 to 500 °C.

Table 20

Urea process

(anatase type, specific surface area: 100 m<sup>2</sup>/g, 0.7 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	400	500
ΔE after ultra-violet ray irradiation for 30 minutes (A)	7.14	8.94
○ ○		
ΔE after leaving in dark place for 60 minutes	3.49	3.70
Restoration factor	52 %	59 %
ΔE after leaving in dark place for 120 minutes	3.01	2.74
Restoration factor	58 %	70 %
ΔE after leaving in dark place for 24 hours (B)	2.37	1.54
○ ○		
Restoration factor	67 %	83 %

Table 21

Urea process

(anatase type, specific surface area: 100 m<sup>2</sup>/g, 1.5 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	400	500
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5	$\Delta E$ after ultra-violet ray irradiation for 30 minutes (A)	5.32	6.25
10	$\Delta E$ after leaving in dark place for 60 minutes Restoration factor	1.82	2.46
15	$\Delta E$ after leaving in dark place for 120 minutes Restoration factor	1.53	2.06
20	$\Delta E$ after leaving in dark place for 24 hours (B) Restoration factor	0.83	1.21
25		○	○
30		85 %	81 %

Table 22

Urea process  
(anatase type, specific surface area: 100  $\text{m}^2/\text{g}$ , 3.0 %  $\text{Fe}_2\text{O}_3$ )

30	Calcinating temperature	400	500
35	$\Delta E$ after ultra-violet ray irradiation for 30 minutes (A)	6.25	6.76
40	$\Delta E$ after leaving in dark place for 60 minutes Restoration factor	3.43	4.10
45	$\Delta E$ after leaving in dark place for 120 minutes Restoration factor	45 %	39 %
50	$\Delta E$ after leaving in dark place for 24 hours (B) Restoration factor	2.98	3.71
		58 %	45 %
		1.75	2.40
		○	○
		72 %	64 %

As is seen from Tables 20 to 22, so far as fine particle titanium oxide is concerned, sufficient photochromic property can be imparted even at a calcinating temperature of about 400 °C.

Amount of active agent added and photochromic property

Researches were conducted concerning the amount of iron oxide added as active agent and photoch-

romic property.

When the amount of the active agent added is increased, coloring is sometimes produced. In this case, the sample is no longer suited for the observation of the photochromic property.

Accordingly, researches and investigations were conducted about the photochromic property in case 5 when the amount of the active agent added is held low.

Test example 1 Synthesis from titanyl sulfate-iron (1)

800 ml of 2 M  $\text{TiOSO}_4$  aqueous solution was prepared, and  $\text{FeCl}_3$  aqueous solution such as to provide 10 three different levels of % by weight of  $\text{Fe}_2\text{O}_3$  with respect to  $\text{TiO}_2$ , i.e., 0.7, 1.5 and 3.0 % were added to the  $\text{TiOSO}_4$  aqueous solution. Subsequently, the resultant system was heated for 4 hours and then cooled down to room temperature, followed by filtering and washing with water. Then, the pH was adjusted to 8 with a  $\text{NaOH}$  aqueous solution, and the system was then washed with water again and dried.

This fine particle titanium oxide was calcinated at 500 to 800 °C.

15 First, anatase type was investigated by varying the amount of  $\text{Fe}_2\text{O}_3$ .

Table 23

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### Urea process

(anatase, specific surface area:  $48 \text{ m}^2/\text{g}$ . 0.7 %  $\text{Fe}_2\text{O}_3$ )

Calcinating temperature	560	600	660	700
$\Delta E$ after ultra-violet ray irradiation for 30 minutes (A)	8.15	7.74	6.85	9.57
$\Delta E$ after leaving in dark place for 60 minutes	3.31	3.91	4.21	7.30
Restoration factor	59 %	49 %	39 %	24 %
$\Delta E$ after leaving in dark place for 120 minutes	2.44	3.31	3.79	6.80
Restoration factor	70 %	57 %	45 %	29 %
$\Delta E$ after leaving in dark place for 24 hours (B)	1.26	1.71	1.94	4.23
Restoration factor	85 %	78 %	72 %	56 %

Table 24

## Urea process

(anatase, specific surface area: 100 m<sup>2</sup>/g, 1.5 % Fe<sub>2</sub>O<sub>3</sub>)

Calcinating temperature	560	600	660	700
$\Delta E$ after ultra-violet lay irradiation for 30 minutes (A)	5.40	5.33	6.98	6.15
	○	○	○	○
$\Delta E$ after leaving in dark place for 60 minutes	2.16	2.39	3.22	3.62
Restoration factor	60 %	55 %	54 %	41 %
$\Delta E$ after leaving in dark place for 120 minutes	1.86	2.33	2.74	2.94
Restoration factor	66 %	56 %	61 %	52 %
$\Delta E$ after leaving in dark place for 24 hours	0.87	0.93	1.15	2.15

(B)	○	○	○	○
Restoration factor	84 %	83 %	84 %	65 %

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Table 25  
Urea process  
(anatase, specific surface area: 100 m<sup>2</sup>/g, 3.0 % Fe<sub>2</sub>O<sub>3</sub>)

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Calcinating temperature	560	600	660	700
ΔE after ultra-violet ray irradiation for 30 minutes	4.82	5.29	5.34	5.83
(A)	△	○	○	○
ΔE after leaving in dark place for 60 minutes	2.77	2.69	3.49	4.44
Restoration factor	43 %	49 %	35 %	24 %
ΔE after leaving in dark place for 120 minutes	2.50	2.42	3.23	4.30
Restoration factor	48 %	54 %	40 %	26 %
ΔE after leaving in dark place for 24 hours	1.16	1.48	1.99	2.71
(B)	○	○	○	○
Restoration factor	76 %	72 %	63 %	54 %

It will be seen that when anatase type titanium oxide is used, excellent photochromic property can be obtained with any amount of Fe<sub>2</sub>O<sub>3</sub>.

Accordingly, researches were made on the status of the photochromic property exhibition using small quantity of active agent.

800 ml of 2 M TiOSO<sub>4</sub> aqueous solution was prepared and FeCl<sub>3</sub> aqueous solutions such as to provide five different levels of % by weight of Fe<sub>2</sub>O<sub>3</sub> with respect to TiO<sub>2</sub>, i.e., 0.01, 0.05, 0.125, 0.25 and 0.5 % were added in the TiOSO<sub>4</sub> aqueous solution. Subsequently, the resultant system was heated for 4 hours and then cooled down to room temperature, followed by filtering and washing with water. Then, the pH was adjusted to 8 with a NaOH aqueous solution, and the system was then washed again with water and dried.

Table 26

600 °C					
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.05	0.125	0.25	0.5
ΔE after ultraviolet irradiation for 30 minutes (A)	2.17 x	4.68 Δ	8.46 ○	10.16 ○	10.20 ○
ΔE after leaving in dark place for 60 minutes	0.65	1.69	5.25	6.75	6.93
ΔE after leaving in dark place for 180 minutes	1.01	0.94	3.70	4.71	5.10
ΔE after leaving in dark place for 24 hours (B)	0.98 ○	0.88 ○	0.27 ○	2.10 ○	1.70 ○
Restoration factor	55 %	81 %	77 %	79 %	83 %

Table 27

700 °C					
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.05	0.125	0.25	0.5
ΔE after ultra-violet ray irradiation for 30 minutes (A)	1.92 x	7.89 ○	7.11 ○	8.31 ○	8.09 ○
ΔE after leaving in dark place for 60 minutes	0.63	5.08	4.38	6.54	6.58
ΔE after leaving in dark place for 180 minutes	0.93	3.89	3.49	5.79	5.64
ΔE after leaving in dark place for 24 hours (B)	0.89 ○	2.32 ○	1.56 ○	3.74 ○	3.23 ○
Restoration factor	54 %	71 %	78 %	55 %	60 %

Table 28

800 °C					
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.05	0.125	0.25	0.5
ΔE after ultra-violet ray irradiation for 30 minutes (A)	1.54 x	4.44 Δ	6.11 ○	5.25 ○	6.34 ○
ΔE after leaving in dark place for 60 minutes	1.05	2.66	3.71	3.54	4.43
ΔE after leaving in dark place for 180 minutes	1.18	2.19	2.89	3.04	3.78
ΔE after leaving in dark place for 24 hours (B)	1.00 ○	1.24 ○	1.49 ○	1.42 ○	1.52 ○
Restoration factor	35 %	72 %	76 %	73 %	76 %

As the result of the above test, it was made clear that when using anatase type titanium oxide, it is suitable to add an active agent by 0.25 to 0.5 % by weight in terms of Fe<sub>2</sub>O<sub>3</sub>.

Low temperature calcinating tests were further conducted on these particularly satisfactorily photochromic samples.

Table 29

500 °C			
5	Fe <sub>2</sub> O <sub>3</sub>	0.25	0.5
	ΔE after ultra-violet ray irradiation for 30 minutes (A)	13.39 ○	17.88 ○
10	ΔE after leaving in dark place for 60 minutes	7.64	13.69
	ΔE after leaving in dark place for 180 minutes	3.02	11.44
	ΔE after leaving in dark place for 24 hours (B)	0.44 ○	6.11 ×
15	Restoration factor	97 %	66 %

Table 30

550 °C			
20	Fe <sub>2</sub> O <sub>3</sub>	0.25	0.5
	ΔE after ultra-violet ray irradiation for 30 minutes (A)	7.39 ○	13.58 ○
25	ΔE after leaving in dark place for 60 minutes	4.42	10.15
	ΔE after leaving in dark place for 180 minutes	1.72	7.96
30	ΔE after leaving in dark place for 24 hours (B)	0.59 ○	3.71 △
	Restoration factor	92 %	73 %

It will be understood that very satisfactory color change degree and restoration factor can be obtained by adding 0.25 % of Fe<sub>2</sub>O<sub>3</sub> as active agent and carrying out calcinating 500 to 550 °C.

35 While the specific surface area of the material titanium oxide is 181 m<sup>2</sup>/g, after calcinating at 600 °C the specific surface area is 45.9 m<sup>2</sup>/g. Thus, the specific surface area is maintained satisfactorily.

#### Photochromic titanium oxide and ultra-violet ray shield effect

40 From the above various experiments, it is made clear that for obtaining excellent photochromic property by calcinating at a comparatively low temperature below 700 °C it is suitable to incorporate 50 % or more of anatase type titanium oxide and incorporate iron, if used as active agent, by about 0.25 % by weight in terms of Fe<sub>2</sub>O<sub>3</sub>.

Meanwhile, the specific surface area and calcinating temperature of titanium oxide are very closely 45 related to each other as noted earlier.

Accordingly, researches were conducted about the correlation between the calcinating temperature and specific surface area.

Fig. 4 shows the relation between the specific surface area and the calcinating temperature.

In the Figure, all the plots have downward slopes toward the right and substantially straight. They can 50 be given as  $S = bT + a$  with  $S$  being the specific surface area of powder after calcinating,  $T$  being the calcinating temperature and  $a$  and  $b$  being constants.

The plot line I shows the relation between the surface area  $S_1$  and temperature  $T$  in case when amorphous titanium oxide of 700 m<sup>2</sup>/g, obtained by the liquid phase process from Ti(O-iso-Pr)<sub>4</sub>, was calcinated at various temperatures.

55 As a result of this regressive analysis, the following relation could be obtained.

$$S_1 = -0.876T + 768.$$

The phantom line plot II shows the relation between the specific surface area  $S_2$  and temperature  $T$  in case when anatase type titanium oxide of  $100 \text{ m}^2/\text{g}$ , obtained by the liquid phase process from  $\text{Ti(O-iso-Pr)}_4$ , was calcinated at various temperatures.

As a result of this regressive analysis, the following relation could be obtained.

5  $S_1 = -0.125T + 140$

The dashed line plot III shows the relation between the surface area  $S_1$  and temperature  $T$  in case when amorphous titanium oxide of  $100 \text{ m}^2/\text{g}$ , obtained by the gaseous phase process from  $\text{TiCl}_4$ , was calcinated at various temperatures.

10 As a result of this regressive analysis, the following relation could be obtained.

15  $S_1 = -0.123T + 129$

20 Further, although not shown, in case when titanium oxide with a specific surface area of  $55 \text{ m}^2/\text{g}$  and with amorphous/rutile = 75/25, obtained by the gaseous phase process from  $\text{TiCl}_4$ , regressive analysis yielded the following relation.

25  $S_1 = -0.10T + 90$

20 Thus, it will be understood that the constant  $a$  assumes a value of the sum of the specific surface area  $S_0$  before the calcinating and about 30 to 70, while the constant  $b$  is reduced substantially in inverse proportion to the specific surface area before the calcinating.

25 In either case, in either plot, when the calculating temperature exceeds  $700^\circ\text{C}$ , the specific surface area is undesirably extremely reduced. Further, regarding fine particle titanium oxide, sufficient photochromic property can be obtained at a temperature not higher than  $700^\circ\text{C}$ , particularly not higher than  $600^\circ\text{C}$ , as noted above. Thus, a suitable calcinating temperature range is  $400^\circ\text{C} \leq T \leq 600^\circ\text{C}$ .

When the material titanium oxide used has a specific surface area of  $100 \text{ m}^2/\text{g}$  or above, sufficient specific surface area and photochromic property can be obtained in a range of  $700^\circ\text{C}$ .

30 When the material titanium oxide used has a specific surface area of  $100 \text{ m}^2/\text{g}$ , it is possible to use  $b = -0.10$  and  $a = S_0 + 35$  ( $S_0$  being the specific surface area of the powder after the calcinating) for satisfactorily calculating the specific surface area of the powder after the calcinating.

35 Thus, with titanium oxide having a specific surface area of  $100 \text{ m}^2/\text{g}$  or below used as material, if the minimum specific surface area of the powder after the calcinating is  $25 \text{ m}^2/\text{g}$ , the upper limit of the calcinating temperature can be calculated from

25 =  $-0.10T + (S_0 + 35)$

$T = (S_0 + 10)/0.10$

40 Accordingly, material titanium oxide containing 50 % or more of anatase type titanium oxide was actually calcinated at  $700^\circ\text{C}$  or below, and the ultra-violet ray shield effect of the calcinated material was investigated.

First, the specific surface area of each photochromic titanium oxide was investigated.

45 Table 31

Material titanium oxide	Specific surface area	Treatment process	$\text{Fe}_2\text{O}_3$	calcinating temperature	Specific area after calcinating	surface
Anatase	98 $\text{m}^2/\text{g}$	Neutralization	0.7%	700 $^\circ\text{C}$	39.2 $\text{m}^2/\text{g}$	
Same	Same	Same	same	660	52.2	
Same	Same	Same	same	600	67.0	
Same	Same	Urea	same	700	40.0	
Same	Same	Same	same	660	47.0	
Same	Same	Same	same	600	68.5	

It will be understood that each sample of calcinated titanium oxide has a specific surface area of 40

$\text{m}^2/\text{g}$  or above, that is, it maintains particle sizes 40 to 70  $\text{m}^2/\text{g}$  in terms of the specific surface area range, which is particularly suitable with respect to the ultra-violet scattering.

Specific researches were conducted concerning the ultra-violet scattering effects.

Samples were prepared as follows.

5

(1) Neutralization process (photochromic ultra-violet ray shield powder samples 1 to 3)

100 g of titanium oxide (anatase type, specific surface area: 98  $\text{m}^2/\text{g}$ ) was dispersed in 2,000 ml of deionized water. Then, 10.5 g of iron chloride  $\text{FeCl}_3$  was added, and the system was stirred. Then, about 10 g of sodium hydroxide was added for neutralization to pH 8 (shield powder sample 1), pH 9 (shield powder sample 2) and pH 10 (shield powder sample 3), followed by reaction at 80 to 90 °C for 2 hours. Then, each system was filtered, and the residue was washed with water and dried. The dry residue was then calcinated at 600 °C and disintegrated. As comparative example, calcinating was effected at 800 °C.

15 Each test sample was diluted to 5 % in a blend solution composed of 95 % of castor oil and 5 % of "Cosmol<sup>T</sup>" (Sorbitan sesqui oleate) and then coated using an applicator to a thickness of 10  $\mu\text{m}$  for measurement.

Fig. 5 shows the ultra-violet ray shield effect.

20 As is clear from the Figure, all the shield powder samples 1 to 3 show excellent shield effect with respect to ultra-violet rays of 300 to 400 nm. There was a trend for the slightly higher effect obtainable with the lower pH.

(2) Urea process (photochromic ultra-violet ray shield powder samples 4 to 6)

40 g of titanium oxide (anatase type, 98  $\text{m}^2/\text{g}$ ) was dispersed in 800 ml of deionized water, then 0.41 g 25 of ion chloride  $\text{FeCl}_3$  was added, and the system was then stirred. Then, a ml of 5 % sodium hydroxide aqueous solution was added for neutralization. Then, 1.29 g of urea was added, and the system was reacted at 90 °C to 98 °C for 3 hours. Then, the samples were filtered, and the residues were washed with water and dried. Then, calcinating was done at 400 °C (sample 4), 600 °C (sample 5) and 700 °C (sample 6), and each sample was then disintegrated. The measurement was done in the same way as with the above 30 samples 1 to 3.

Fig. 6 shows the ultra-violet ray shield effect.

As is clear from the Figure, the more excellent ultra-violet ray shield effect is obtainable with the lower calcinating temperature.

35 (3) Urea process (photochromic ultra-violet ray shield powder samples 7 and 8)

Titanium oxide (anatase type, 100  $\text{m}^2/\text{g}$ ) was prepared such that  $\text{Fe}_2\text{O}_3$  was 0.7 %, and then calcinated at 560 °C (sample 7), and 600 °C (sample 8).

Fig. 7 shows the ultra-violet ray shield effect of the photochromic ultra-violet ray shield powder samples.

40 It will be seen that in this case very excellent ultra-violet ray shield effect can be obtained compared to the cases of Figs. 5 and 6.

Now, examples of the manufacture of the photochromic ultra-violet ray shield powder according to the invention will be described.

45 Example 1

While stirring a solution obtained by diluting 100 parts of titanium tetra-iso-propoxide with 500 parts of iso-propanol, a solution obtained by diluting 50 parts of water with 500 parts of iso-propanol was added for hydrolysis.

50 To this suspension was added a solution obtained by dissolving 5 parts of ferrous chloride in ethanol, and the resultant system was subjected to a surface treatment with its pH adjusted to about 10 using sodium hydroxide. This suspension was condensed using suction filter means, and then dried at 120 to obtain 40 parts of stable fine particle powder with a specific surface area of about 700  $\text{m}^2/\text{g}$ .

55 This fine particle powder was calcinated at the following temperatures. As a result the following specific surface areas and photochromic properties could be obtained.

Table 32

Calcinating temperature	400	500	600	700
Specific surface area	475.7	278.6	197.3	165.2
$\Delta E$ after ultra-violet ray irradiation for 30 minutes (A)	6.39 ○	5.94 ○	5.02 ○	3.42 x
$\Delta E$ after leaving in dark place for 60 minutes	2.56	2.59	3.86	2.56
$\Delta E$ after leaving in dark place for 120 minutes	2.27	2.29	2.39	2.35
$\Delta E$ after leaving in dark place for 24 hours (B)	1.16 ○	1.20 ○	1.70 ○	1.21 ○
Restoration factor	81	% 79	% 66	% 64 %

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Example 2

Anatase type titanium oxide with a specific surface area of 100 m<sup>2</sup>/g was produced from TiOSO<sub>4</sub> by the liquid phase process, and photochromic ultra-violet ray shield powder was produced by using 1.5 % of Fe<sub>2</sub>O<sub>3</sub> as an active agent.

The following specific surface areas and photochromic properties could be obtained.

Table 33

Calcinating temperature	450	500	550	600	700
Specific surface area	67.3	61.6	55.9	58.4	37.6
$\Delta E$ after ultra-violet ray irradiation for 30 minutes (A)	6.39 ○	5.62 ○	5.49 ○	5.99 ○	7.77 ○
$\Delta E$ after leaving in dark place for 60 minutes	3.52	3.25	3.26	3.60	5.61
$\Delta E$ after leaving in dark place for 120 minutes	3.08	2.95	3.01	3.25	5.18
$\Delta E$ after leaving in dark place for 24 hours (B)	1.88 ○	1.74 ○	2.12 ○	1.98 ○	3.21 △
Restoration factor	71 %	70 %	62 %	67 %	59 %

Fig. 8 shows specific ultra-violet ray shield effects.

In the Figure, the relation between the ultra-violet ray shield degree and the wavelength is shown in cases of calcinating temperatures of 450, 500, 550, 600 and 700 °C. It will be seen from the Figure that while all the samples have excellent ultra-violet ray shield effects, the more satisfactory effects can be obtained the lower the calcinating temperature.

As for the difference in the effect between the urea process and the neutralization processes, the effect was slightly better with the neutralization process, but the difference was not so much.

Example 3

In a first trough 100 parts of tetra-iso-propoxy titanium was heated at about 200 °C, in a second trough 500 parts of water was heated at about 120 °C, and air was introduced from each trough as carrier gas into an electric furnace at 600 °C for hydrolysis. Further, in a third trough 1.5 parts of zinc chloride was heated at about 800 °C, and air was introduced from the trough into the same electric furnace for surface treatment. This powder was recovered using filter cloth to obtain 40 parts of material anatase type titanium oxide with a specific surface area of 100 m<sup>2</sup>/g.

This powder was calcinated at 500 °C to obtain photochromic ultra-violet ray shield powder with A = 5.05, B = 2.01 and specific surface area of 79.0 m<sup>2</sup>/g.

Examples of the composition using the photochromic ultra-violet ray shield powder as above according to the invention are given below. Each composition showed excellent photochromic property and ultra-violet ray shield effect.

Composition example 1 Pressed powder	
(1) Photochromic ultra-violet ray shield powder (sample 4)	5.2%
(2) Talc	90.0%
(3) Iron oxide	2.5%
(4) Squalane	2.0%
(5) Preservative agent	0.2%
(6) Perfume	0.1%

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## (Method of manufacture)

The components (1) to (3) were mixed, and in this mixture the components (4) to (6) were thermally dissolved. The resultant system was disintegrated. The resultant particles were molded into the form of dishes, thus obtaining pressed powder.

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Composition example 2 Powder foundation	
(1) Photochromic ultra-violet ray shield powder (sample 7)	20.0%
(2) Talc	10.0%
(3) Sericite	47.9%
(4) Spherical nylon powder	8.0%
(5) Red iron oxide	0.5%
(6) Yellow iron oxide	1.0%
(7) Black iron oxide	0.1%
(8) Polydimethyl siloxane	5.0%
(9) 2-ethylhexyl palmitate	5.0%
(10) Sorbitan sesquioleate	1.5%
(11) Preservative agent	0.9%
(12) Perfume	0.1%

35

40

## (Method of manufacture)

The components (1) to (9) were mixed using a Henshell Mixer mixer. To this mixture was added what was obtained by thermally dissolving and mixing the components (9) to (12). The resultant system was disintegrated using a Pulverizer (by Hosokawa Mikuron). The resultant particles were then molded into the form of a dish, thus obtaining a powder foundation.

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Composition example 3 Dual purpose foundation	
(1) Photochromic ultra-violet ray shield powder (sample 1)	5.0%
(2) Silicone-treated mica	46.25%
(3) Silicone-treated talc	25.0%
(4) Silicone-treated iron oxide	4.5%
(5) Silicone-treated titanium oxide	6.5%
(6) Trilmethylolpropane triisostearate	5.0%
(7) Squalane	3.0%
(8) Bees was	2.0%
(9) Sorbitan Trioleate	1.0%
(10) Preservative agent	0.5%
(11) Vitamin E	0.05%
(12) Butylmethoxybenzoin methane	1.0%
(13) Perfume	0.2%

## (Method of manufacture)

The components (1) to (5) were mixed. To this mixture was added what was obtained by thermally dissolving the components (6) to (13). The system was then disintegrated. The obtained particles were molded to the shape of a disk to obtain a dual foundation.

Composition example 4 sun oil		
(1) Liquid paraffin	69.75%	
(2) Silicone oil	20.0%	
(3) Vitamin E	0.05%	
(4) Perfume	0.2%	
(5) Photochromic ultra-violet ray shield powder (sample 8)	10.0%	

15 (Method of manufacture)

The components (1) to (4) were mixed, and then the component (5) was added and dispersed. Then, the system was degassed to obtain sun oil. The sun oil was darkened when exposed to sunlight, and also it has excellent ultra-violet ray shield effect.

Composition example 5 paint		
(1) Photochromic ultra-violet ray shield powder (sample 8)	2.0%	
(2) Acryloid B-66	22.0%	
(3) Xylene	56.0%	
(4) Mineral spirit	20.0%	

30 (Method of manufacture)

The components (1) to (5) were needed with a mill to obtain acrylic acid paint.

Composition example 6 Emulsified foundation		
(1) Photochromic ultra-violet ray shield powder (sample 7)	1.0%	
(2) Stearic acid	1.5%	
(3) Isostearic acid	0.3%	
(4) Isopropyl myristate	4.0%	
(5) Squalane	12.0%	
(6) POE stearylether	1.5%	
(7) Glyceryl monooleate	0.5%	
(8) Cetylalcohol	0.5%	
(9) Talc	10.0%	
(10) Iron oxide	0.5%	
(11) Preservative agent	0.15%	
(12) Triethanol amino	0.8%	
(13) Propylene glycol	6.0%	
(14) Montmorillonite	0.5%	
(15) Refined water	60.55%	
(16) Perfume	0.2%	

55 (Method of manufacture)

The components (12) to (15) Were mixed and heated to 70 °C. Then, the components (1) to (9) were mixed and disintegrated to be added to the first-mentioned mixture. Then, the oil components (2) to (8), (11) and (16), which were preliminarily thermally dissolved and mixed at 70 °C, were gradually added. Then the system was subjected to emulsified dispersion. The resultant system was cooled down to room temperature

to obtain an emulsified foundation.

### Claims

5 1. A photochromic ultra-violet ray shield powder principally composed of particles with specific surface areas of  $25 \text{ m}^2/\text{g}$  or above and  $A \geq 5$  and  $B \leq 3$ , said A and B being determined as follows.  
 10 4 g of said powder is uniformly dispersed in 16 g of nitrocellulose lacquer to form a dispersion, which is coated on art paper using an applicator to form a coating film with thickness of  $76 \mu\text{m}$ , which coating film is in turn dried to be used as a sample for photochromic property measurement under an optical condition that a lamp ("FL20S.BLB" manufactured by Toshiba) and a lamp ("FL20S.E" manufactured by Toshiba) are secured at a distance of 11 cm from each other. Distance adjustment of the sample is effected using an ultra-violet ray intensity measuring apparatus ("SUV-T" manufactured by Tolay Techno) such that the intensity of ultra-violet rays incident on the sample is  $2 \text{ mW/cm}^2$ .  
 15 (1) The sample is colorimetrically measured after it has been left at room temperature and in a dark place for about 10 hours, the measurement being made using a colorimeter ("CR-200" manufactured by Minolta).  
 (2) The sample is immediately colorimetrically measured when it is darkened by irradiation with said ultra-violet rays for 30 minutes in the same way as described above.  
 20 (3) The irradiated sample is similarly colorimetrically measured after leaving it at room temperature and in a dark place for 24 hours.  
 A represents the color difference  $\Delta E$  between the color determined in (1) and the color determined in (2).  
 B represents the color difference  $\Delta E$  between the color determined in (1) and the color determined in (3).  
 25 2. The photochromic ultra-violet ray shield powder according to claim 1, which is principally composed of titanium oxide.  
 30 3. The photochromic ultra-violet ray shield powder according to claim 2, which contains at least 50 % of anatase type titanium oxide.  
 4. The photochromic ultra-violet ray shield powder according to claim 2, which contains a photochromic property imparting agent metal Me such that  
 35  $0.05 \geq \text{MeO}_m/(\text{MeO}_m + \text{TiO}_2) \geq 0.0001$   
 $m = 1/2, 1, 3/2, 2$  or  $3$ .  
 5. A photochromic ultra-violet ray shield powder obtainable by calcinating material titanium oxide with a specific surface area of  $100 \text{ m}^2/\text{g}$  or above at a temperature of  $700^\circ\text{C}$  or below.  
 40 6. A method of manufacturing photochromic ultra-violet ray shield powder comprising the step of calcinating material titanium oxide with a specific surface area  $S_0 \text{ m}^2/\text{g}$  ( $S_0$  being 100 or below) at a temperature of  $T^\circ\text{C}$  calculated by relations (1) below;  
 Relations (1):  
 45 
$$T = (S_0 + 10)/0.10$$
  

$$400 \leq T \leq 600$$
  
 7. The method according to claim 6, wherein said photochromic property imparting agent metal is in the form of salt or alkoxide and precipitated by solution of said salt or said alkoxide by neutralization or hydrolysis reaction.  
 50 8. The method according to claim 7, wherein the pH is controlled to 8 to 11 during the neutralization.  
 55 9. A skin external preparation containing 0.1 to 60 % by weight of the photochromic ultra-violet ray shield powder according to claim 1.

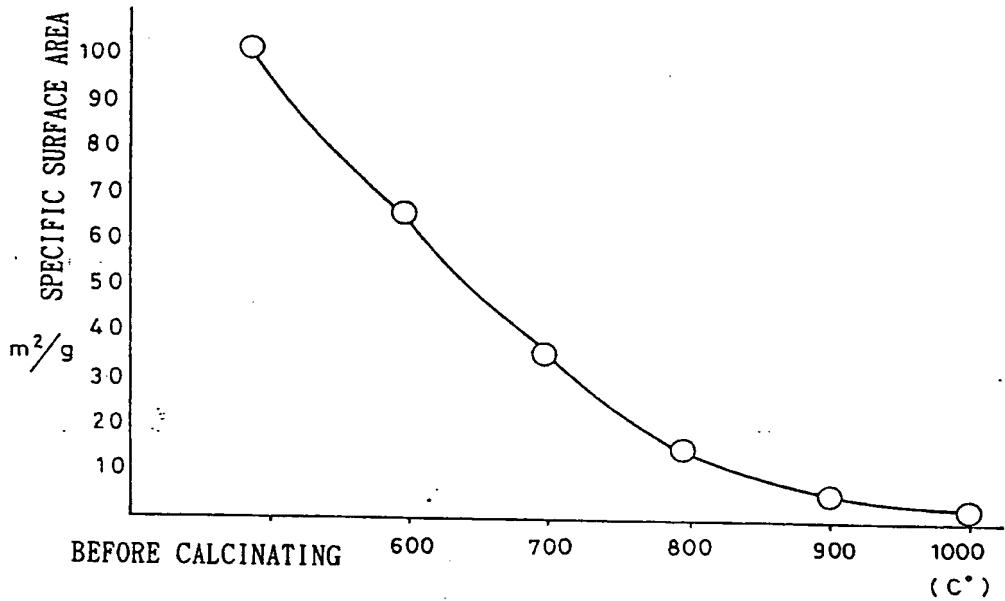


Fig. 1

## NEUTRALIZATION PROCESS

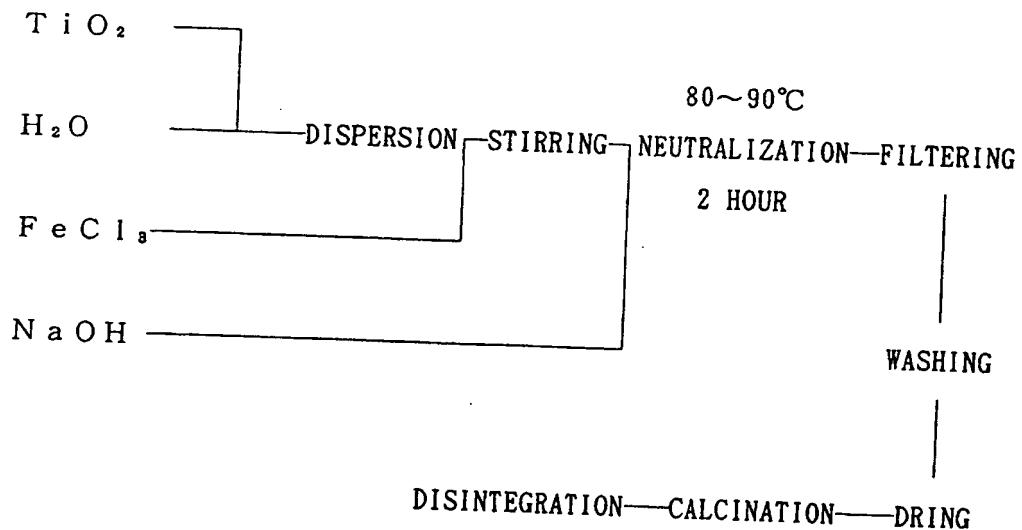


Fig. 2

UREA PROCESS

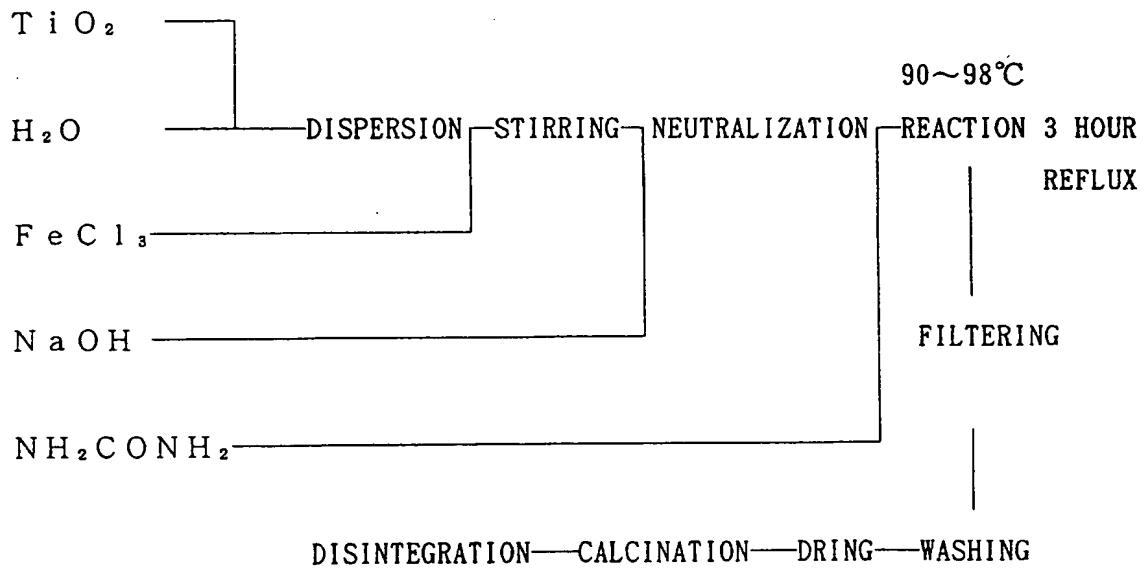


Fig. 3

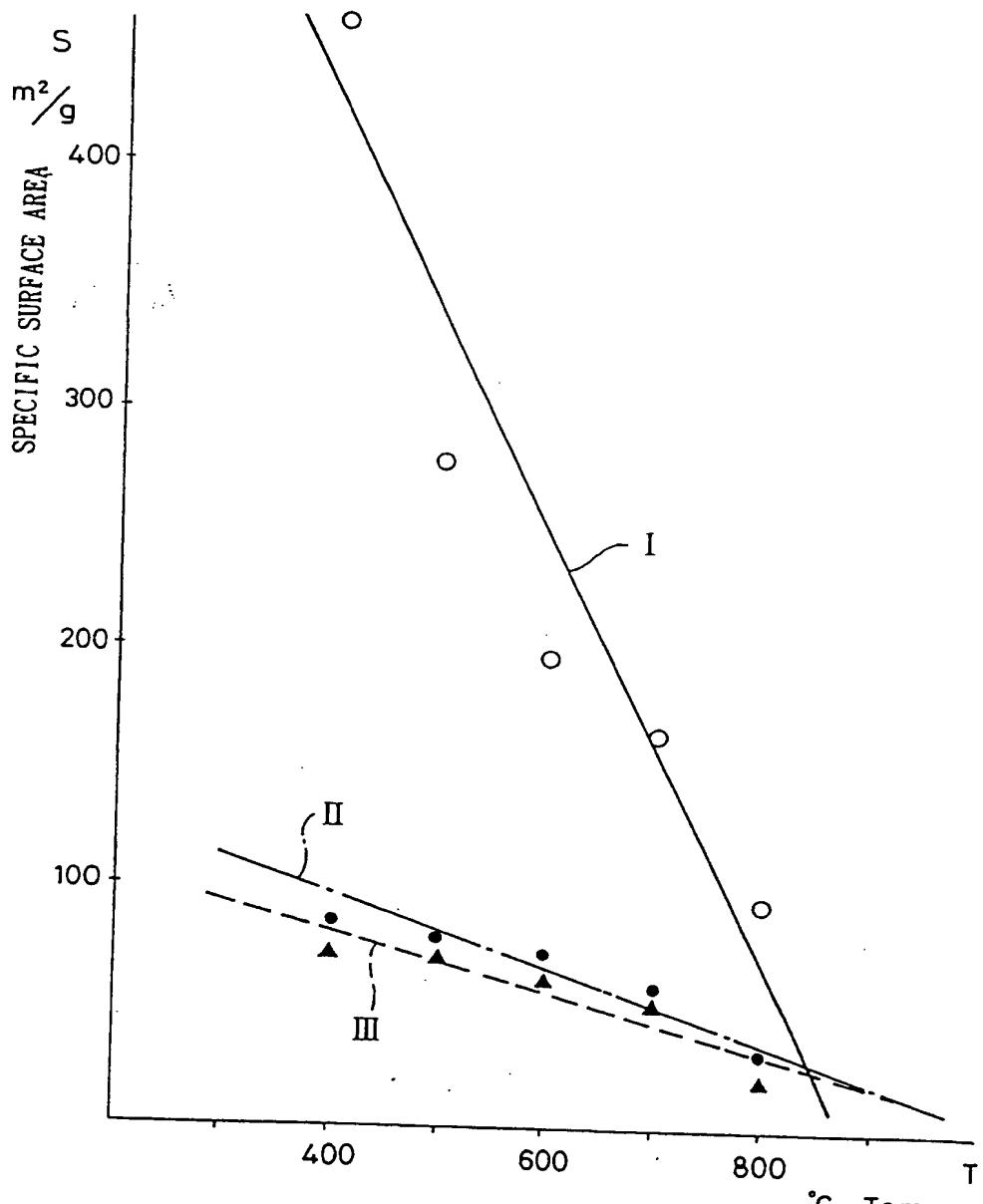


Fig. 4

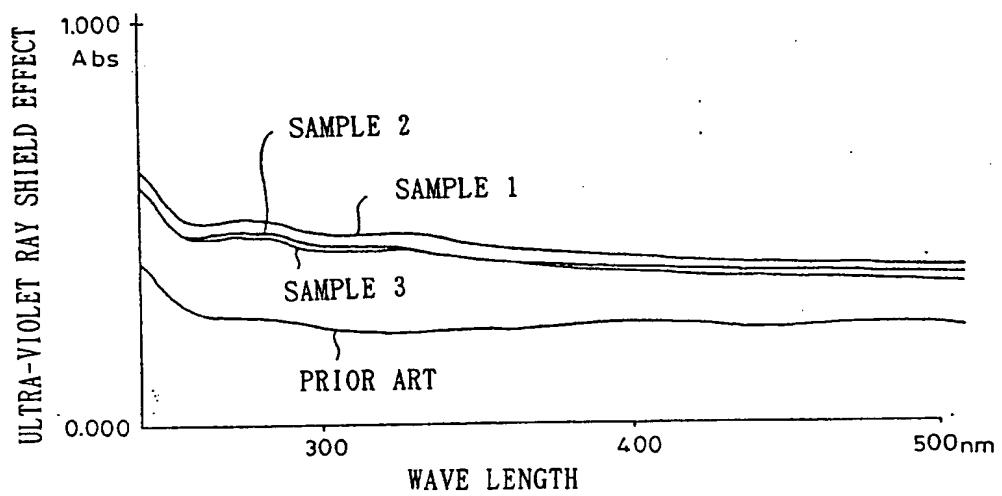


Fig. 5

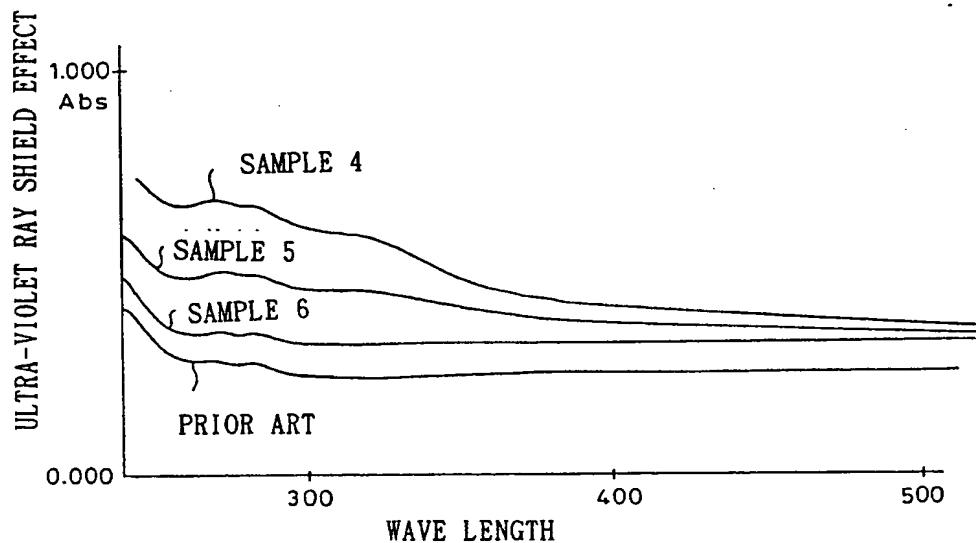


Fig. 6

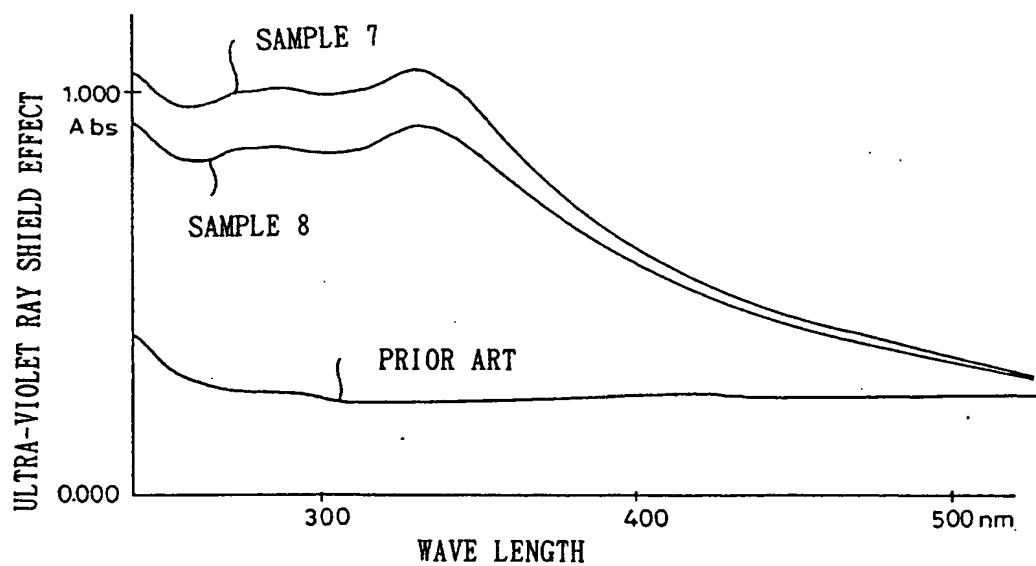


Fig. 7

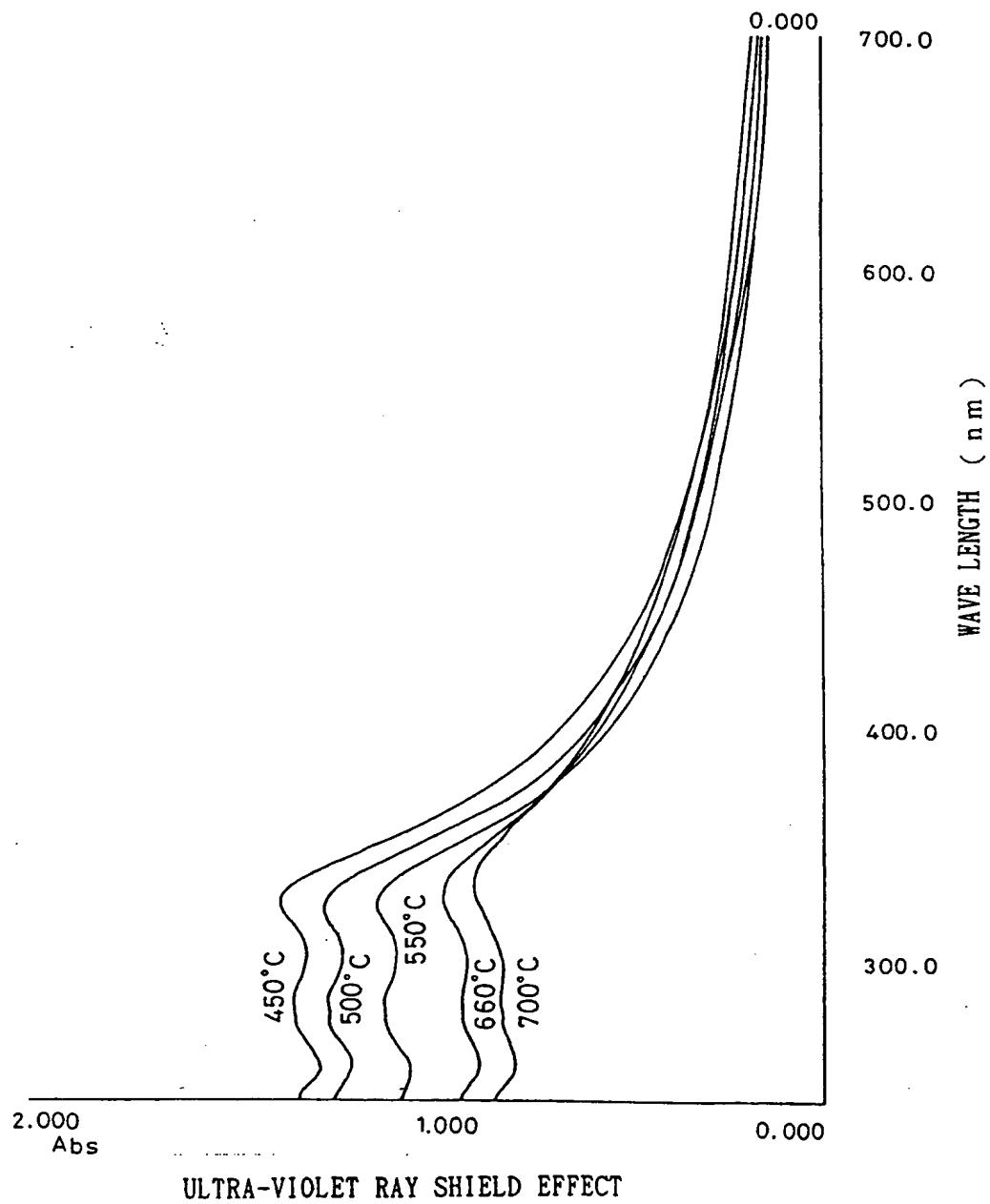


Fig. 8



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Application Number

EP 92 10 9768

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
Category	Citation of document with indication, where appropriate, of relevant passages				
D, A	EP-A-0 359 909 (SHISEIDO COMPANY LIMITED) * the whole document *---	1-4, 9	A61K7/42 A61K7/00 C09C1/36 A61K7/02		
A	DE-A-4 038 258 (SHISEIDO CO. LTD.) * the whole document *---	1-4, 9			
P, A	DATABASE WPIL Week 9226, Derwent Publications Ltd., London, GB; AN 92-211973 & JP-A-4 139 109 (KOBAYASHI KOSE KK) 13 May 1992 * abstract *---	1-4, 9			
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 387 (C-536)(3234) 14 October 1988 & JP-A-63 132 811 ( SHISEIDO CO. LTD. ) 4 June 1988 * abstract *---	1-4, 9			
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 267 (C-443) & JP-A-62 067 014 ( SUNSTAR INC. ) 26 March 1987 * abstract *---	1-4, 9	TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
P, X	EP-A-0 444 798 (KEMIRA OY) * the whole document *-----	5-8	A61K C09C		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	01 OCTOBER 1992	COUCKUYT P.J.R.			
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